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# REACTION OF TERTIARY PHOSPHINE DICHLORIDES WITH THIOLS IN THE PRESENCE OF TRIETHYLAMINE. A CONVENIENT METHOD FOR THE REDUCTION OF PHOSPHINE OXIDES TO PHOSPHINES

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The reaction of phosphine dichlorides with 1- or 2-alkanethiols or benzenethiol in the presence of triethylamine and subsequent distillation afforded phosphines and disulfides in good yields. The reaction was shown to be useful for reduction of tertiary phosphine oxides to the corresponding phosphines.

Tertiary phosphine dihalides, which are readily derivable from tertiary phosphine oxides,1) can be reduced to the corresponding phosphines. The known reagents for the reduction are inorganic materials including phosphorus,2) hydrazine,3) metal hydrides,4) and various metals5) or organometallic compounds, such as butyllithium and phenylmagnesium bromide.6) We wish report here the reaction of tertiary phosphine dichlorides with thiols in the presence of tertiary amine yielding the corresponding phosphines and disulfides in good yields (Eq. 1). This reaction provides a useful method for converting phosphine oxides into phosphines.

$$R_3PCl_2 \quad + \quad 2\ H\text{-}SR' \xrightarrow[-2\ HCl]{2\ Base} \xrightarrow{Distn.} R_3P \quad + \quad (R'S)_2 \qquad \text{Eq. 1}$$

Tributyl- or triphenyl-phosphine dichloride could be most conveniently prepared <u>in situ</u> by the treatment of the respective phosphine oxide with an equimolar amount of oxalyl chloride (OxCh, Eq. 2) or a half molar amount of trichloromethyl chloroformate (TCF, Eq. 3) in benzene or toluene. A typical procedure for the

$$R_3PO \quad + \quad (COCl)_2 \longrightarrow R_3PCl_2 \quad + \quad CO \quad + \quad CO_2 \qquad \text{Eq. 2}$$

$$2\ R_3PO \quad + \quad ClCOOCCl_3 \longrightarrow 2\ R_3PCl_2 \quad + \quad 2\ CO_2 \qquad \text{Eq. 3}$$

reduction is the following.

A solution of oxalyl chloride (5.08 g, 40 mmol) in benzene (20 ml) was added drop by drop to a solution of tributylphosphine oxide (8.73 g, 40 mmol) in benzene (80 ml) at room temperature, thereby a vigorous evolution of gas occurred. Total amount of the gas evolved was ca. 1820 ml. To the resulting suspension of tributylphosphine dichloride were added drop by drop a solution of ethanethiol (4.97 g, 80 mmol) in benzene (20 ml) and subsequently a solution of triethylamine

(8.09 g, 80 mmol) in benzene (20 ml) at room temperature. After removal of the resulting triethylamine hydrochloride by filtration, the mixture was stripped of solvent under reduced pressure. The residue was then distilled. The yields of the products are recorded in Table 1.

Table 1 Reduction of Phosphine Oxide

| Reactants | | | Yields of Products (%) | | | |
|---|---|---|---|---|---|---|
| $R_3PO$ | Chlorinating Agent | R'SH | $NEt_3 \cdot HCl$ | $R_3P$ | $(R'S)_2$ | $R_3PS$ |
| $Bu_3PO$ | OxCh | EtSH | 95 | 77 | 70 | 6 |
| $Ph_3PO$ | OxCh | EtSH | 86 | 53 | 53 | 24 |
| $Bu_3PO$ | TCF | i-PrSH | 98 | 84 | 81 | trace |
| $Ph_3PO$ | OxCh | BuSH | 82 | 49 | 57 | 36 |
| $Bu_3PO$ | TCF | $C_8H_{17}SH$ | 95 | 83 | 78 | 3 |
| $Bu_3PO$ | TCF | PhSH | 100 | 68 | 77 | 0 |
| $Ph_3PO$ | OxCh | PhSH | 100 | 87 | 100 | 0 |

The best yields of tertiary phosphines were obtained by the use of 2-propanethiol or 1-octanethiol for tributylphosphine dichloride and benzenethiol for triphenylphosphine dichloride, respectively.

The reaction of tertiary phosphine dihalides with alkanethiols in the absence of tertiary amine results in formation of alkyl halides and phosphine sulfides.$^{7)}$

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